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(19) (CA) **CANADIAN PATENT** (12)

(54) ON LINE HYDROTREATING TO PRODUCE FINISHED PRODUCTS

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ABSTRACT

Raw shale oil containing precipitable compounds such as iron and arsenic are preheated to below the precipitation temperature and then mixed with hot recycled hydrogen and oil, and catalytically hydrocracked in an ebullated bed catalytic reactor. The metal compounds are deposited on the catalyst in the reactor, from which they are withdrawn along with used catalyst which is replaced with fresh catalyst. The reactor effluent is further hydrotreated in a fixed-bed catalyst reactor, usually at extreme conditions of 780-830°F and 1800-2500 psig hydrogen partial pressure. The resulting material is phase-separated and distilled to provide jet and diesel fuel oil product meeting military specifications, while clean hydrogen and heavy oil streams are reheated and recycled to the ebullated bed reactor.

UPGRADING HEAVY OIL WITH ON-LINE HYDROTREATING
TO PRODUCE FUEL PRODUCTS

BACKGROUND OF INVENTION

Field of Invention:

This invention pertains to processing hydrocarbon feedstocks containing precipitable impurities which deposit out during conventional preheating, and pertains particularly to processing raw shale oil containing depositable metallic compounds to produce catalytically hydroprocessed fuels suitable for jet and diesel engine usage.

Description of Prior Art:

It has been observed that when raw shale oil is catalytically hydrogenated to produce improved lighter oil products, the preheating equipment passages are usually fouled by fine particulate deposits from the shale oil at temperatures above about 400°F. Such deposits produce high pressure drop and even plugging of flow passages and are very troublesome and undesirable. Specific problems which are encountered during hydrotreating operations on shale oil feedstock include repeated fouling preheater flow passages by particulate deposits at temperatures above approximately 400°F, and fouling the fixed-bed catalytic reactor by very fine particulate deposits having high iron content, causing excessive pressure drop and inadequate oil conversion.

These deposits are evidently from chemical compounds which contain principally iron and arsenic compounds which cannot be readily filtered out of the liquid feedstream at ambient temperature conditions. Thus, a solution has been



sought for avoiding or preventing such contaminant problems in processing raw shale oil, so as to permit continuous catalytic processing of such oils to produce upgraded fuel products.

Multi-stage catalytic processing of heavy petroleum crude oils and residuum is known. For example, U.S. 3,705,849 to Alpert discloses a process for desulfurization of petroleum residuum feedstocks using ebullated catalytic bed hydrogenation reactors in series to reduce hydrogen consumption and increase catalyst life. U.S. 3,773,653 to Nongbri and U.S. 3,788,973 to Wolk disclose similar multi-stage catalytic conversion processes for petroleum residuum. Also, U.S. 3,887,455 to Hammer discloses a process for hydrotreatment of heavy crudes and residua using ebullated catalytic beds or fixed-bed reactors in series, using catalyst having smaller pore size in the second reactor.

U.S. 4,046,670 to Seguchi discloses a process for thermal cracking heavy petroleum oil in tubular-type heating furnace, and wherein an inorganic substance containing iron oxide is added to the feed as an anti-clogging agent. U.S. 4,181,596 to Jensen discloses treating shale oil retort effluent to lower pour point and reduce contaminants, such as soluble arsenic and iron, by cooling the effluent and maintaining the liquid phase in a critical temperature range of 600-800°F for 1-120 minutes.

Also, U.S. 4,158,622 to Schwarzenbek discloses a two-stage hydrogenation process for hydrocarbons containing particulate fines such as shale oil, utilizing an ebullating bed catalytic reactor from which the vapor portion is passed to a stationary bed reactor for further hydrotreatment. Despite this prior activity, a need still exists for processing raw shale oil which contains precipitable inorganic materials and compounds so as

to avoid fouling of equipment passages and catalytic beds and provide improved operations.

SUMMARY OF INVENTION

This invention provides a method for preheating hydrocarbon feedstocks containing precipitable compounds which cause flow passage fouling problems, and for hydroprocessing such hydrocarbon liquids such as raw shale oil to produce upgraded fuels suitable for jet and diesel usage. The hydrocarbon feed is heated indirectly to a moderate temperature below which any precipitation of inorganic compounds occurs, such as about 400-600°F, and is then passed to an ebullated catalyst first stage bed reaction step for initial hydroprocessing. The resulting effluent liquid is phase separated and the vapor portion is passed to one or more fixed catalytic bed hydrotreating steps usually operated at more severe conditions; i.e., at higher temperature and pressure conditions, or lower space velocity, for further processing.

The specific process steps include preheating the feed; e.g., raw shale oil, to a temperature at least about 350°F to separate sediment and water, but avoiding a temperature at which precipitation and fouling occurs in the preheater flow passage. Then, passing the heated feedstream with hydrogen to a first stage hydrocracking operation using an ebullated catalyst bed type reactor to provide further feed stream heating via the heat of hydrogenation and depositing the precipitated solids on the catalyst.

The recycle hydrogen stream and/or a heavy recycle oil fraction, such as about 650°F+ are heated sufficiently to make up the additional heating to achieve a reaction temperature of

over about 750°F in the ebullated catalyst bed unit. Useful reaction conditions are 800-860°F temperature, 1800-3000 psig hydrogen partial pressure, and space velocity of 0.7-3 Vf/hr/Vr.

Following an initial catalytic hydrogenation step in an ebullated bed reactor, it has been unexpectedly found that by further processing heavy feedstocks such as shale oil in a down-flow fixed bed catalytic hydrotreater operated at extreme conditions of temperature and pressure, remarkably high quality products can be produced even in the presence of high partial pressure of H_2S and NH_3 . The extreme conditions employed are temperatures in excess of 780°F and hydrogen partial pressures in excess of 1800 psig. This temperature produces some further hydrotreating which allows the liquid products of this operation, boiling below 510°F, to meet military specification for JP-4 jet and diesel fuels. This hydrotreating step also facilitates denitrogenation of the product.

Operations conducted on processed raw shale oil having a nitrogen content of about 1.27 W % and a sulfur content of 0.75 W % have produced fuel oil products having a nitrogen content of less than 4 ppm and a sulfur content less than 0.01 W % to meet JP-4 fuel specifications.

DESCRIPTION OF THE DRAWING

Figure 1 is a schematic flowsheet of a two-stage catalytic reaction process using indirect heating of a hydrocarbon feedstream upstream of an ebullated catalyst bed hydrogenation step, followed by further catalytic hydrotreating in a fixed bed reactor.

DESCRIPTION OF PREFERRED EMBODIMENTS

As shown in Figure 1, raw shale oil feedstock at 10 is heated in heater 12 to a temperature below which contained inorganic compounds precipitate, such as 350-400°F and not above about 600°F, using a convenient source of heat such as low Btu gas. Sediment and water are removed at 13. The preheated oil 14 is introduced with hydrogen 15 into an ebullated bed catalytic reactor unit 16. The reactor has provision for fresh catalyst addition either with the feed at 14a or by addition into the reactor vessel at 17 and withdrawal of used catalyst at 18 as shown. Reaction conditions are usually 825-860°F temperature, 2000-2600 psig hydrogen partial pressure, and liquid hourly space velocity within the range of 0.7-1.5 Vf/hr/Vr. The reactor contains ebullated bed 16a of particulate catalyst. Suitable catalyst is commercially available cobalt-molybdenum or nickel-molybdenum on alumina support and having a narrow particle size within the broad range of 0.003 to 0.060 inch. Catalyst and solids are withdrawn either from the reactor at connection 18 or with non-vaporized product from the hot separator 20. Reactor effluent stream 19 is passed to hot separator 20, from which vapor stream 21 is passed to hydrotreater 30. Hot separator liquid at 22 is flashed in two stages 24 and 26 at successively lower pressure, and the resulting combined vapors 23 are passed to vapor product line 27. The residual liquid 28 from the last flash step 26 is partially recycled to the reactor for further cracking, and the remainder 2a burned as fuel or discarded.

The resulting hydrocarbon-containing stream at 27 is introduced directly to downflow fixed-bed catalytic hydrotreater 30 with hydrogen at substantially the same high temperature and pressure conditions existing from reactor 16. In the hydrotrea-

ter 30, which is preferably operated at extreme hydrotreating conditions of 800-825°F temperature range, 1800-2500 psig hydrogen partial pressure, and space velocity of 0.8-1.5 Vf/hr/Vr, the vapor product is further cracked and virtually completely desulfurized and denitrogenated.

Suitable catalyst is nickel-molybdenum or alumina support and having particle size of 0.060-0.125 inch. The reaction temperature will increase through the catalyst bed due to the exothermic reaction. Hydrotreater 30 may be comprised of two or more catalyst beds in series, with the temperature rise in the beds being controlled by injecting cool hydrogen gas between the beds such as at 30a.

The resulting product 31 is cooled at 32 and phase separated at 34. The resulting liquid portion is pressure-reduced at 35 and fractionated at 36 into fuel gas 37, naphtha at 37a, jet fuel at 38, and diesel fuel products at 38a. Any naphtha produced is suitable for catalytic reforming to produce gasoline. From fractionator 36, the heavier liquid fraction, such as 650°F+, at 39 is heated to above 800°F at heater 51 and recycled to the reactor unit 16 for further processing.

The effluent vapor stream 33 from phase separator 34 is separated at 40 to remove contaminants such as C₁ to C₃ gases, H₂S, and NH₃ at 42. Hydrogen at 41 is compressed at 44, heated at 45 to 850-1000°F, and recycled directly to the reactor 16. The C₁ and C₃ gases at 43 from separation step 40, along with some natural gas make up at 49, are reformed at 50 to make additional hydrogen stream 46 as needed in the process.

It is pointed out that the important features of this process for upgrading hydrocarbon feedstock such as shale oil are (a) limiting the preheating of the feedstock and supplying the additional heat by heating the hydrogen and clean recycled

heavy liquid fraction, and thus avoiding the precipitation of deposits in the feed preheater flow passages, (b) precipitation of inorganic compounds on the catalyst in the ebullated bed reactor, and (c) on-line catalytic hydrotreating step operated at extreme conditions to produce finished liquid fuel products. The clean recycled heavy product fraction and hydrogen are separately heated using fired heaters to provide the necessary heat to the ebullated bed catalytic reaction. These process steps as well as other features of the process are applicable to coal, heavy oil and tar sand bitumen processing, as well as to preferably processing raw shale oil to produce refined fuel oils products.

This invention is further illustrated by reference to the following examples, which should not be construed as limiting the scope of the invention.

EXAMPLE 1

Upgrading operations were conducted with raw shale oil containing 1.6 W % nitrogen, 20 ppm arsenic, 60 ppm iron and about 0.06 W % ash impurities. The oil was preheated in a tubular exchanger to about 700°F, and passed with hydrogen to a downflow-type catalytic reactor containing a fixed bed of commercially available nickel catalyst particles for hydrotreatment. Pressure drop across the preheater tube increased from about 10 psi to 200 psi over 12 days, so that operations had to be discontinued and the heater coil replaced. Analysis of the material deposited in the coil and also in the top of the reactor bed indicated it was about 38 W % oil and 62 W % ash, containing 2 W % carbon, 45 W % iron and 6.3 W % arsenic.

EXAMPLE 2

Further upgrading operations are conducted using the same raw shale oil feedstock as in Example 1. However, the oil is preheated in a tubular heat exchanger to only about 450°F, and then passed into the bottom of an upflow-type reactor containing as ebullated bed of commercially available cobalt molybdenum catalyst extrudate particles. Recycle hydrogen gas is heated to 925-950°F and heavy 650°F+ recycle oil is heated to 800-825°F and also introduced into the bottom of the reactor. The reaction zone conditions are maintained within the range of 825-850°F temperature, 2000-2600 psig partial pressure of hydrogen, and space velocity of about 1.2 Vf/hr/Vr. An effluent stream is removed from the upper end of the reactor and passed to further processing steps to recover product oil. The iron and arsenic impurities are substantially deposited on the catalyst particles in the reactor and are removed with the used catalyst, thus avoiding difficulties with precipitation of such contaminants from the shale oil feed causing increased pressure drop and operating problems in the process, and permitting continuous extended operations.

EXAMPLE 3

The preheated effluent stream from the ebullated bed catalyst reactor of Example 1, containing nitrogen content of about 0.9 W % is passed on to a second stage fixed-bed catalytic reactor for further processing. The oil is hydrotreated at inlet conditions of 800-825°F temperature and 1800-2000 psig partial pressure of hydrogen by passing over a suitable hydrotreating catalyst, usually nickel-molybdenum on alumina support at space velocity of

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about $1.0 \text{ } V_f/\text{hr}/V_r$. The resulting hydrotreated oil product has increased API gravity, a nitrogen content of less than about 4 ppm and sulfur content less than about 0.01 W %, thus making it suitable as high quality fuel for jet and diesel engine use.

Although we have disclosed certain preferred embodiments of our invention, it is recognized that modifications may be made theretowithin the spirit and scope of the disclosure and as defined solely by the following claims.

1. A method for preheating heavy hydrocarbon feedstock containing precipitable metal compounds to a reaction zone comprising:

- (a) heating the hydrocarbon feed to a temperature below the precipitation temperature of the metal compounds and introducing it into the reaction zone containing an ebullated catalyst bed;
- (b) heating a recycled hydrogen stream and a recycled heavy oil stream produced in the process to temperature above the reaction zone temperature, and introducing said heated streams into the reaction zone to help provide the desired temperature therein; and
- (c) depositing the precipitating components from the feedstock onto the catalyst in the reaction zone.

2. The process of Claim 1, wherein used catalyst containing precipitated metal compound deposits is withdrawn from the reaction zone and replaced with fresh catalyst.

3. The method of Claim 1, wherein the reaction zone temperature is maintained at 800-860°F, the recycle hydrogen stream is heated to 850-1000°F, and the heavy recycle oil is heated to 800-850°F before introducing said streams into the reaction zone.

4. The process of Claim 1, wherein the hydrocarbon feed is raw shale oil containing metal compounds, and said feed is preheated in step (a) to temperature not exceeding about 600°F.

5. The process of Claim 1, wherein the effluent from the ebullated catalyst bed reaction zone is passed to a fixed-bed catalytic hydrotreating step for further processing.

6. A process for hydrotreating a hydrocarbon feedstream containing precipitable metal compounds, comprising the steps of:

- (a) preheating the hydrocarbon feedstream to temperatures below the precipitation temperature of the metal com-

pounds and introducing the heated feed with hydrogen into a reaction zone containing an ebullated catalyst bed;

- (b) maintaining the reaction zone at 800-860°F temperature and 1800-3000 psig hydrogen partial pressure to hydrocrack and treat the feed and deposit the precipitable compound onto the catalyst particles;
- (c) further hydrotreating the effluent vapor portion from said reaction zone in a fixed-bed catalytic reactor, maintained at 780-825°F temperature and 1800-3000 psig hydrogen partial pressure;
- (d) recovering a hydrogen-containing gas stream, a hydrocarbon liquid product stream, and a heavy hydrogen liquid stream;
- (e) purifying said hydrogen-containing stream, reheating the hydrogen to 850-1000°F temperature, and introducing it into the ebullated bed reaction zone to help maintain the temperature therein; and
- (f) reheating the heavy hydrocarbon liquid stream to 800-850°F and introducing it also into the ebullated bed reaction zone to help maintain the reaction temperature therein.

7. The process of Claim 6, wherein the feedstream is raw shale oil which is preheated to temperature not exceeding about 600°F.

8. The process of Claim 6, wherein the contaminant material precipitated and deposited on catalyst in step (b) is withdrawn from the ebullated bed catalytic reaction zone along with used catalyst, and is replaced with fresh catalyst.

9. The process of Claim 6, wherein the ebullated bed first reaction zone is maintained at 825-860°F temperature, 1800-2800 psig hydrogen partial pressure, and space velocity of $0.5-3 \text{ } V_f / \text{hr}$.

10. The process of Claim 6, wherein the catalyst used in fixed-bed reactor hydrotreating step (e) is nickel-molybdenum on alumina support.

11. A process for hydrocracking and hydrotreating heavy raw shale oil feedstock containing a contaminant which precipitates at temperatures below the reaction temperature, which comprises:

- (a) preheating the hydrocarbon feedstream to a temperature of 400-600°F and introducing the heated stream with heated hydrogen into a first reaction zone containing an ebullated catalyst bed;
- (b) reacting the feedstock in the ebullated bed first reaction zone at 800-860°F temperature and 1800-3000 psig hydrogen partial pressure conditions, and allowing the precipitable material to deposit on the catalyst in the bed;
- (c) withdrawing used catalyst containing precipitated arsenic and iron contaminant from the first reaction zone, and replacing the used catalyst with fresh catalyst;
- (d) passing the reaction zone effluent on to a second reaction zone having a fixed catalytic bed maintained at 780-830°F temperature for further hydrotreating the feed;
- (e) recovering a hydrogen-containing gas stream, a hydro-treated shale oil liquid product stream, and a heavy hydrocarbon liquid stream;
- (f) purifying said hydrogen-containing stream and reheating the hydrogen to 850-1000°F temperature and introducing it into the ebullated bed reaction zone to help maintain the temperature therein; and
- (g) reheating the heavy hydrocarbon liquid stream to 800-850°F and introducing it into the ebullated bed reaction zone to help maintain the reaction temperature therein.



